PRELIMINARY STUDY OF THE EXCHANGE OF CARBON ATOMS BETWEEN CARBON MONOXIDE AND GRAPHON

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The exchange of C atoms between CO and Graphon samples has been studied. Samples between zero and 36% burn-off and temperatures between 800 and 950° were used. ^{13}C was employed as a tracer and mass spectroscopy as the analytical tool. The exchange followed a simple kinetic scheme. It was possible to measure the concentration of active sites, rate constants, and the activation energy for the exchange, which was found to be 55 kcal/mole between 800 and 850°. The concentration of active sites was found to be quite variable from sample to sample, with the major determining factor being the exact conditions under which the previous increment of burn-off had been performed rather than the actual degree of burn-off. Following exchange, gasification of the surface with O_2 was used to retrieve the ^{13}C deposited on the surface during the exchange. Major factors influencing the ease of retrieval were found to be sample burn-off and the temperature of exchange.

Introduction

Little attention has been paid to the exchange of carbon atoms between CO and elemental carbon. Brown[1] showed that when sugar, charcoal or graphite was exposed to ^{14}CO at temperatures above 700°, the carbon surface acquired radioactivity, which could not be removed by evacuating the sample at 1000° or by treatment of the sample with boiling water or hot acids. He concluded that ^{14}C atoms were deposited on the surface by an exchange reaction. Kanter[2] prepared natural graphite crystals with ^{14}C on the surface by exchange with ^{14}CO at 1575°. Dominey et al.[3] investigated the exchange between ^{14}CO and PGA graphite at temperatures in the region of 2000°, with the intention of producing uniformly labelled graphite. Lang & Magnier[4] measured the mobility threshold of carbon atoms in the graphite lattice by means of the ^{14}CO-graphite exchange kinetics and found that exchange becomes rapid above 1700°, which also corresponds to the threshold of graphitisation.

All the work that has been described has involved the ^{14}C isotope, the concentration of which has been measured by radioactivity techniques. Work in this laboratory was started by Miles, (unpublished results) using the stable isotope ^{13}C, the exchange reaction being followed by use of a mass spectrometer. He found that at 848° an exchange of C atoms would take place between a 0·1109 g sample of 20·8% burn-off Graphon and a mixture of 53·9% ^{13}CO and 46·1% ^{12}CO of total pressure 65 mtorr in a 1·04 l system. During the exchange reaction, ^{13}C atoms from the gas phase were deposited on the surface of the Graphon. He investigated possible methods of removing the deposited ^{13}C from the surface and found that exposure of the surface to normal CO at 850° would cause the deposited ^{13}C to exchange with the ^{12}CO in the gas phase, causing a partial retrieval of the deposited ^{13}C. He also found that the deposited ^{13}C could be removed by reacting the Graphon with O_2, although complete removal of the deposited ^{13}C was not obtained even after several percent burn-off.

The work which is described in this paper was undertaken with the intention of using the technique developed by Miles to further investigate the kinetics of the exchange reaction and to examine the factors which influence the ease of retrieval of the deposited C atoms.

Experimental

Materials

The carbon used in this study was a sample of Spheron 6, a fine particle channel black supplied by the Cabot Corporation, Boston, Massachusetts, which had been graphitised by F. M. Lang of Commissariat a l'Energie Atomique, Saclay, France, at a temperature of over 3000° with the intention of obtaining an ultrapure carbon. Total ash content was found to be 25–35 ppm. The material was similar to the Graphon used extensively in this laboratory, which had been graphitised between 2700 and 2800°. The B.E.T. (accepted test for surface area: Brunauer, Emmett & Teller J. Am. chem. Soc., 1938, 60, 309) area of this sample provided by Lang was 74 m²/g, compared with 76 m²/g for the 2700° Graphon sample. X-ray diffraction patterns for the two materials were almost identical.

The O_2 used was research grade, supplied by Air Products and Chemicals Co., Allentown, Pennsylvania. The major specified impurities were N_2 (11 ppm), Ar (5 ppm) and water (0·76 ppm). The CO sample was the same as used by Miles. It analysed 53·9 mole % ^{13}CO and 46·1 mole % ^{12}CO.

Apparatus

A schematic diagram of the apparatus is shown in Fig. 1. The Graphon sample was placed in a fused quartz bucket suspended in a vertical fused quartz reaction tube. The reaction tube was double walled and the annular volume enclosed by the double wall was evacuated to prevent diffusion into the reaction tube from the atmosphere at the highest temperature used in this study. The tube was heated by an electric furnace, the temperature of which was controlled by a Leeds and Northrup temperature controller, using a chromel–alumel thermocouple placed in close proximity to the sample. Two bulbs were incorporated in order to

Fig. 1. *Schematic diagram of apparatus*

Fig. 2. *Deposition of* ^{13}C *during selected exchange reactions at 850°C*

$\triangle$ 2G; $\square$ 1D; $\bullet$ 2F; $\bigcirc$ 2C
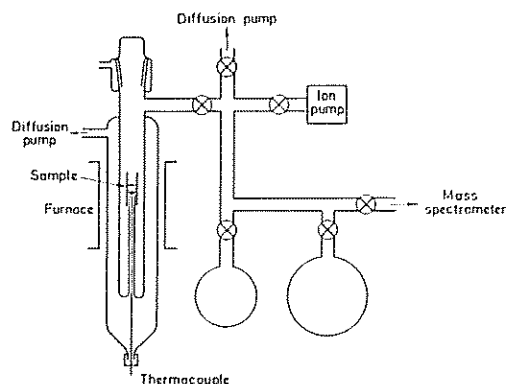
increase the total volume of the system. With the exception of the reaction tube, the reaction system was constructed of Pyrex glass. Glass stopcocks were lubricated with Apiezon 'H' grease. Two different pieces of apparatus were used. The first had a total volume of 19·8 l, which could be reduced to 6·8 l by isolating the larger expansion bulb. The second had a total volume of 19·3 l, which could be reduced to 6·3 l by isolating the larger expansion bulb. The reaction system was evacuated initially by a 20 l/sec oil-diffusion pump backed by a rotary oil pump, and then by an 8 l/sec Ultek ionisation pump to an ultimate vacuum of 10^{-8} torr.

The reaction system was connected to a modified General Electric mass spectrometer through a molecular leak. The mass spectrometer was used to monitor the partial pressures of the gaseous components in the reaction system during a reaction. The leak rate was very low; thus it was found unnecessary to correct for the small amount of gas lost through the leak. The inlet system of the mass spectrometer was used to introduce gases into the reaction system.

Results and Discussion
Exchange attempts

Two samples of Graphon (0·300 g in each case) were used, both from the batch supplied by Lang; they were designated 1 and 2. Four attempts at exchange were made with sample 1, designated 1A, 1B, 1C and 1D. Eight attempts at exchange were made with sample 2, designated 2A, 2B, 2C, 2D, 2E, 2F, 2G and 2H. A reaction system of total volume 6·8 l was used for the exchange attempts with sample 1, while a reaction system of 6·3 l was used with sample 2.
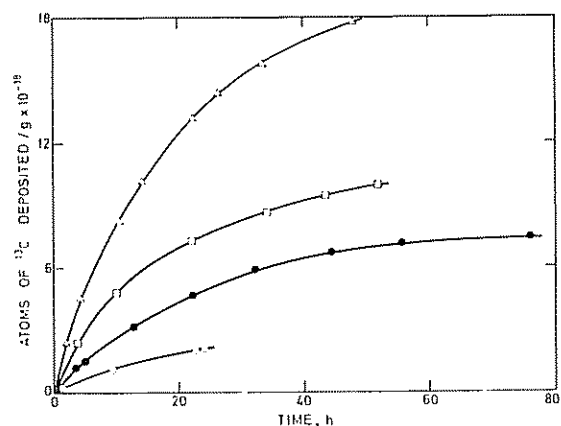
The exchange attempts with samples 1 and 2 were made at intervals during an investigation of the factors which influence the product ratio of the reaction of Graphon with oxygen.[5,6] This investigation required a large number of successive reactions under differing conditions – pressures of O_2 between 10 and 500 mtorr and temperatures between 300 and 675°. Each of these Graphon–O_2 reactions caused a small degree of burn-off. In most cases a temperature of 850° was selected initially to study the exchange, although in some cases the temperature was eventually raised to encourage the exchange to occur more rapidly. The data for each exchange attempt are shown in Table I.

After introduction of the isotopic mixture, the mass spectrometer was used to monitor the ratio of the mass 28 ($^{12}CO^+$) and the 29 ($^{13}CO^+$) ion peaks as a function of time. The total pressure of CO remained constant, indicating that no appreciable chemisorption of CO took place, and furthermore that no disproportionation of CO took place, which was confirmed by the absence of CO_2.

Exposure of the Graphon sample for long periods at temperatures above 850° caused a trace of H_2 to be formed. This was attributed to water vapour desorbing from the walls of the reaction system and reacting with the carbon surface, that is $C + H_2O \rightarrow CO + H_2$.

For each exchange experiment begun at 850°, the number of ^{13}C atoms deposited on the surface as a function of time was calculated. Representative results are shown in Fig. 2. It can be seen that if the exchange is allowed to proceed for an extended period of time, the amount of ^{13}C deposited appears to approach an asymptote, meaning that the net exchange approaches zero even though the isotopic ratio in the gas phase is very different from that in the bulk of the Graphon, or on the B.E.T. surface of the Graphon. It is important to note that although the initial CO starting pressure and

isotopic distribution were approximately the same for each of the runs in Fig. 2, the amount of exchange varied greatly. There is no direct relationship between the amount of exchange and the degree of burn-off.

The cessation of the net exchange was attributed to the achievement of equilibrium in a reversible reaction. Miles showed that the ^{13}C deposited on the surface during the exchange was capable of back-reacting with ^{12}CO. The reversibility of the reaction was further demonstrated in experiment 2E. After the initial exchange reaction had been allowed to proceed for 92 h, by which time the net exchange had practically ceased, the CO was removed from the system and 50 mtorr of the initial isotopic mixture was introduced. Further exchange was seen to take place, and a new equilibrium was approached. The achievement of equilibrium after a very small deposition of ^{13}C atoms (compared with the number necessary to occupy fully the B.E.T. area) indicates that exchange took place with just a few particularly active sites. That is, the activated Graphon samples have a surface area of about 100 m²/g, or about 2×10^{21} carbon sites/g. Thus the ^{13}C is depositing on only about 1% of the B.E.T. surface under the conditions used.

On the basis of a reversible exchange reaction which will eventually achieve equilibrium, a simple kinetic scheme was worked out and the results were applied to the experimental data.

Analysis of the kinetics of exchange

It is supposed that the Graphon sample has N sites per gram which are capable of taking part in the reaction. As normal carbon contains 98·9% ^{12}C and 1·1% ^{13}C, of the N sites per gram 0·989N will be ^{12}C and 0·011N will be ^{13}C. Let $^{13}C_d$ be the number of ^{13}C atoms deposited per gram of sample at time t. The rate of the forward reaction will be:

$$\frac{d^{13}C_d}{dt} = kp_{^{13}CO}(0·989N - {}^{13}C_d)$$

The rate of the back reaction will be:

$$-\frac{d^{13}C_d}{dt} = k'p_{^{12}CO}(0·011N + {}^{13}C_d)$$

On the assumption that $k = k'$, it can be shown that if almost all the reaction system is at 25°:

$$\frac{1}{\dfrac{Nm}{3·24 \times 10^{13}V} + p_{^{12}CO} + p_{^{13}CO}} \times$$

$$\log[1 - ({}^{13}C_d/{}^{13}C_{d\infty})] = -kt \quad \ldots\ldots\ldots\ldots(1)$$

where m is the weight of the sample in grams, V is the volume of the reaction system in ml, $p_{^{12}CO}$ and $p_{^{13}CO}$ are expressed in mtorr, and $^{13}C_{d\infty}$ is the equilibrium amount of ^{13}C deposited on the surface. Further:

$$N = \frac{(p_{^{12}CO} + p_{^{13}CO}) {}^{13}C_{d\infty}}{0·989\,p_{^{13}CO\infty} - 0·011\,p_{^{12}CO\infty}} \quad \ldots\ldots(2)$$

Application of the kinetic scheme to the experimental data

From the graph of $^{13}C_d$ against time, a rough estimate was made of the equilibrium value of $^{13}C_d$, that is $^{13}C_{d\infty}$. Using this value, a graph was drawn of log

$[1 - ({}^{13}C_d/{}^{13}C_{d\infty})]$ against time. If this yielded a curve, the value of $^{13}C_{d\infty}$ selected was adjusted until the best possible straight line was obtained. The value of k was calculated from the gradient of the line, using Equation (1); and N was calculated from the optimum value of $^{13}C_{d\infty}$, using Equation (2). A typical graph of log $[1 - ({}^{13}C_d/{}^{13}C_{d\infty})]$ against t is shown in Fig. 3. The calculated values of N and k are shown in Table 1.

It will be noted that the calculated values of N vary widely, whereas the values of k are fairly constant at about $1·1 \times 10^{-7}$ mtorr^{-1} sec^{-1} site^{-1}, for Graphon samples of burn-off greater than 5%. For burn-offs below this value, the values of k seem to be a little higher.

The variation in N was surprising, since the only apparent variable was the degree of burn-off; and there was no clear dependence of N on the degree of burn-off. The latter may be important, but there is clearly some other factor of overriding importance. It was eventually realised that more important than the degree of burn-off could be the precise way in which the previous incremental burn-off had been performed. It was noted that a high value of N was found when the previous oxidation had been slow. It would, therefore, appear that low temperature gasification of the Graphon surface is required for the production of sites which are active in the exchange reaction.

In run 2H, the exchange was begun at 800°, but after 24 h the temperature was increased to 850°. The graph of log $[1 - ({}^{13}C_d/{}^{13}C_{d\infty})]$ against t is shown in Fig. 4.
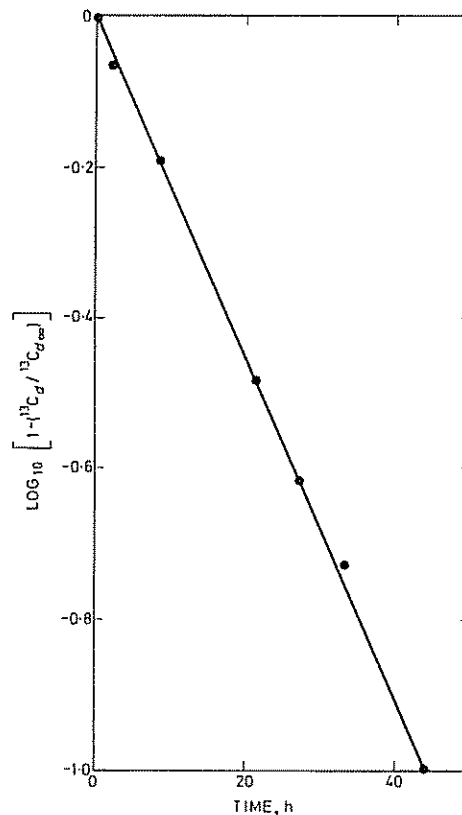

Fig. 3. *Plot of Eq. (1) to determine rate constant for exchange at 850°c. Run 2D*

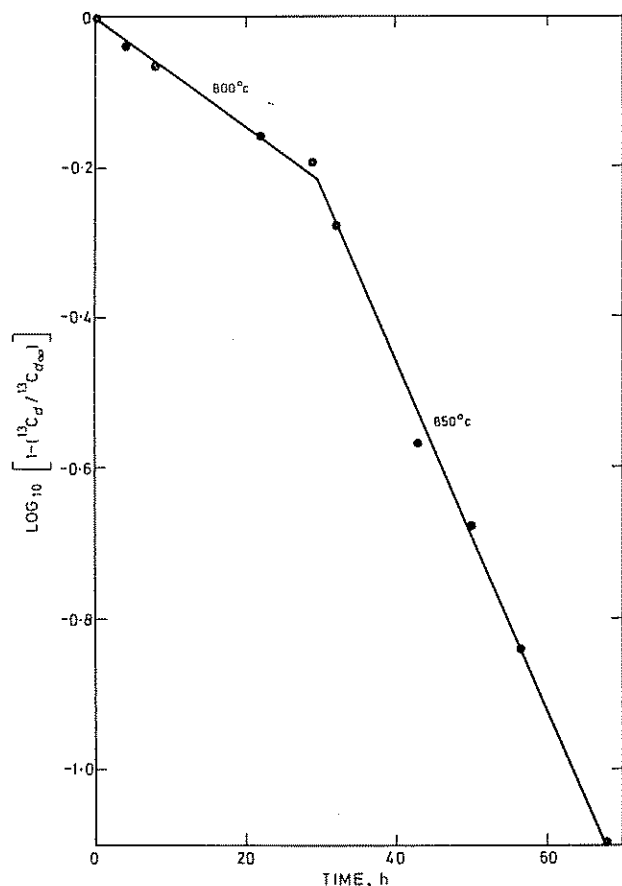Fig. 4. *Plot of Eq. (1) to determine rate constants for exchange at 800 and 850°c. Run 2H*

Fig. 5. *Deposition of ^{13}C during exchange in one run at increasing temperatures of 850, 900, 950°c. Run 2F*

Note that the same value of $^{13}C_{d\infty}$ produces straight-line plots for both the 800 and 850° exchange. From the gradients at the two temperatures, an activation energy of about 55 kcal/mole is calculated.

Exchange at temperatures above 850°

Although in every case the initial temperature used for the exchange was 850° or less, in some cases the temperature was eventually raised above 850°. This was done in exchanges 1C, 2C and 2F.

The simple theory as described previously would suggest that once equilibrium is reached, a change in temperature would not affect it, since the rates of the forward and back reactions will be changed equally. Experimentally this was not found to be the case. In exchange 2F, a very close approximation to equilibrium was attained at 850°, but increasing the temperature to 900° and eventually to 950° caused further deposition of ^{13}C to take place. A graph showing the deposition of ^{13}C against time for exchange 2F is shown in Fig. 5.

The reason for the extra exchange that takes place at the higher temperatures is not entirely clear. A number of possibilities were considered. Firstly, the ^{13}C atoms deposited on the surface may be able to migrate away from active sites by a slow surface diffusion process. This process could be negligibly slow at 850° but considerable at higher temperatures. Experiments which
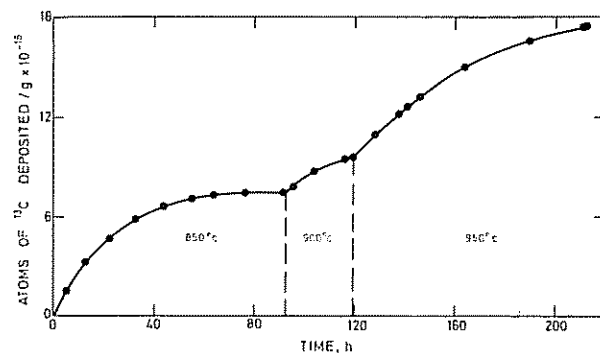
will be described in a later section make this explanation unlikely. A second possibility is that some of the active sites lie in micropores and require an activated diffusion process for reaction to take place. These sites could have a negligible activity at 850° but could become increasingly active as the temperature is raised. A third possibility is that there is more than one type of active site. At 850° exchange takes place primarily on the more active type of site, and an equilibrium is established for these sites. If the temperature is then raised, the less active sites will begin to react slowly.

Experiments involving oxidation of the Graphon surface following deposition of ^{13}C

Following each exchange reaction, the ^{13}C deposited on the surface during the reaction was removed by oxidation of the Graphon. Three different types of schedules were employed:

(i) Low temperature oxygen chemisorption, complex decomposition, gasification by O_2, and finally complex decomposition (see Fig. 6).

(ii) Gasification by O_2 followed by complex decomposition (see Fig. 7).

(iii) Gasification by O_2 in seven sequential reactions, with complex decomposition only after the last reaction (see Fig. 8).

Table II lists the experimental conditions for each of the experiments. The partial pressures of ^{12}CO, ^{13}CO, $^{12}CO_2$ and $^{13}CO_2$ were measured for each of the desorptions and reactions and the extent of removal of the deposited ^{13}C calculated. The results are adjusted for the natural abundance of ^{13}C.

The ease of retrieval of deposited ^{13}C is seen to be quite variable. Low temperature oxygen chemisorption and decomposition of the surface-oxygen complex is the most effective method of recovering deposited ^{13}C. Ease of retrieval is also encouraged by low burn-off. Another factor which appears to be important is the final temperature of exchange. It is seen that the initial retrieval in run 2F is slower than in run 2G, Fig. 7. The degree of burn-off in both cases is similar (28% and 32% respectively); and the total amount of ^{13}C deposited during the exchange reaction is almost identical. The only major difference between the two samples is that in the case of 2F most of the ^{13}C was deposited at 950°, while in the
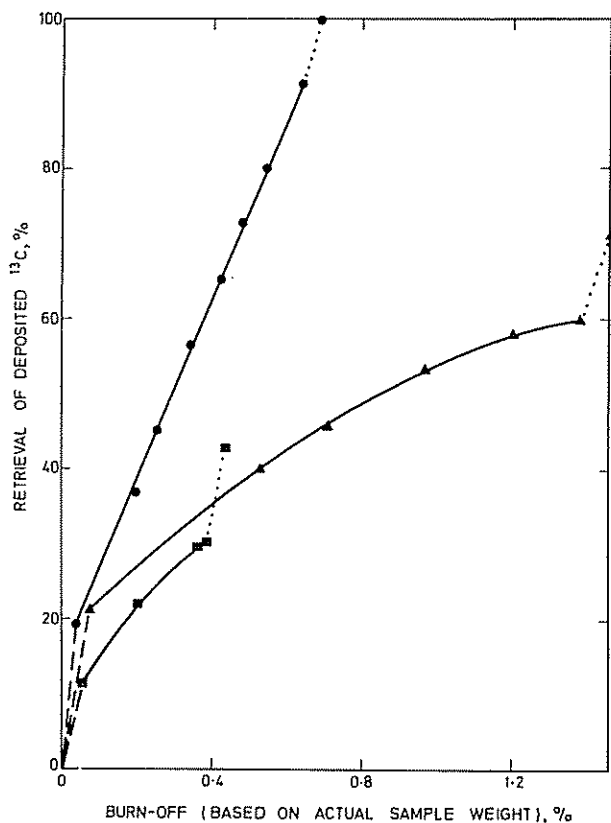
Fig. 6. *Retrieval of deposited* ^{13}C *by a combination of gasification in* O_2 *and complex decomposition for selected runs using Schedule* (i)

— · — · — Decomposition of complex formed at 300°c
————— Gasification
········· Decomposition of complex formed during gasification
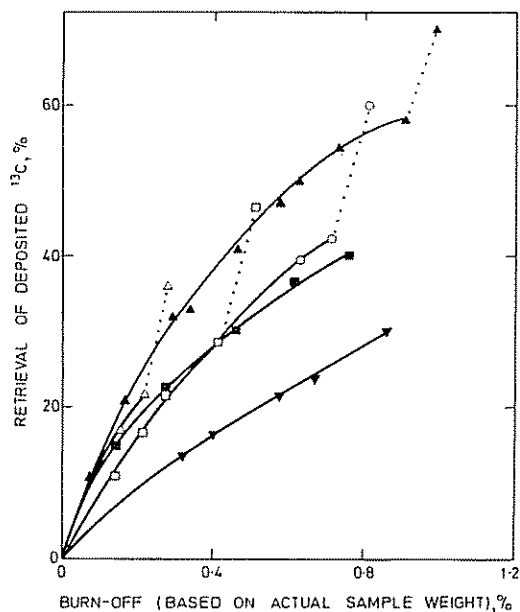
● Run IA; ▲ Run 2D; ■ Run 2E

Fig. 8. *Retrieval of deposited* ^{13}C *by a series of gasification runs and then complex decomposition using schedule* (iii)

————— Gasification
— — — — Decomposition of surface complex formed during gasification

TABLE II

Conditions used for ^{13}C removal by oxygen

Schedule	Run No.	300°c Chemisorption pressure, mtorr	Gasification conditions	
			Press., mtorr	Temp., °C
(i)	1A	500	100	625
(i)	2D	500	200	625
(i)	2E	500	100	625
(ii)	1C	*	100	575
(ii)	1D	*	100	625
(ii)	2C	*	200	575
(ii)	2G	*	100	575
(ii)	2H	*	100	575
(iii)	2F	*	100†	575†

* No chemisorption prior to reaction
† Gasification conditions for each of seven sequential reactions

case of 2G it was all deposited at 850°. It appears that ^{13}C deposited at 950° is more difficult to retrieve than ^{13}C deposited at 850°. The difficulty of retrieval of ^{13}C deposited at 950° raised the question of whether the effect required exchange to take place at this temperature or whether exchange at 850° followed by evacuation of the isotopic mixture and then heating at 950° for an extended period would have the same effect. This was studied in run 2H. Following exchange at 850°, the

Fig. 7. *Retrieval of deposited* ^{13}C *by a combination of gasification and complex decomposition for selected runs using schedule* (ii)

————— Gasification
········· Decomposition of complex formed during gasification

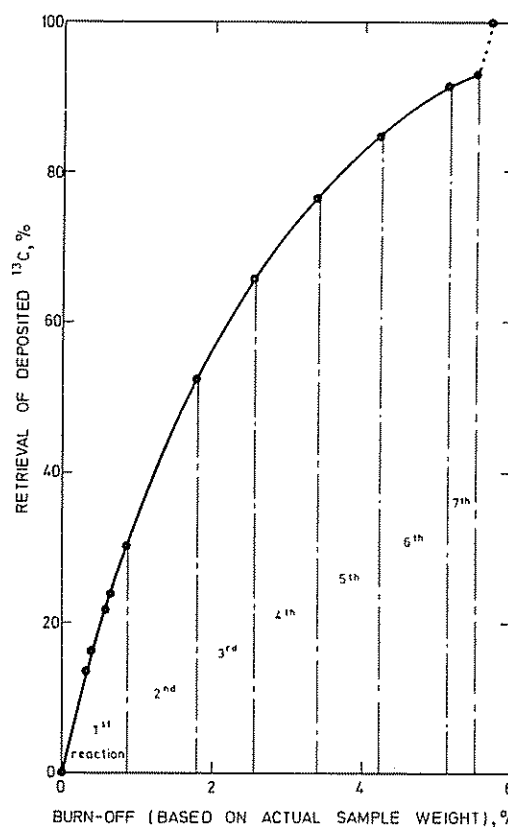△ Run 1C; ■ Run 1D; ▲ — Run 2C; ▼ Run 2F; ○ Run 2G; □ Run 2H

isotopic mixture was evacuated and the sample was then heated in vacuum for 42 h at 950° to see whether this would affect the subsequent retrieval of deposited ^{13}C. The result, as seen in Fig. 7, would suggest that the heating period in vacuum at 950° had not affected the ease of retrieval, making the migration theory suggested previously unlikely.

Schedule (iii) was used only in the case of run 2F. Following exchange, seven successive reactions were performed, all at 575°, each with a starting pressure of 100 mtorr (except for the third when by accident 87 mtorr was used). After each burn-off increment, the product gases and the unused O_2 were evacuated and a new charge of O_2 was introduced. The retrieval as a function of burn-off is shown in Fig. 8. After the seventh reaction, the surface oxide which had been formed was decomposed and at this stage virtually all the ^{13}C originally deposited had been retrieved. The measured parameters for the various reactions were compared. The empirical rate constant was seen to decrease in subsequent reactions although there was very little difference between the values for the third and subsequent reactions. This suggests that during the second and third reactions there was an increase in the amount of surface complex which blocked active sites. The incremental product ratio for ^{12}C, that is $^{12}CO/^{12}CO_2$, was substantially the same for each reaction. A slight decrease had been expected owing to the increase in surface-complex formation which took place,[5] but this was too small to be measurable. A noteworthy aspect was that after the third reaction the graph of $p_{12_{CO}}$ against $p_{12_{CO_2}}$ passes through the origin instead of forming (on extrapolation) an intercept on the $p_{12_{CO}}$ axis. This intercept has been related to the formation of surface oxide.[5] The product ratio for excess ^{13}C increased somewhat during successive reactions, suggesting that sites which generated excess $^{13}CO_2$ were removed a little more readily than those generating excess ^{13}CO, perhaps because they were less likely to be blocked by surface complex at the reaction temperature.

The decomposition of the surface complex after the seventh reaction showed that the total amount of complex formed during the seven reactions was considerably higher than would be expected to be formed during one reaction under these experimental conditions, and this adds further evidence for an increase in stable complex formation during the second and third reactions. The isotopic composition of the decomposition products of the complex was $^{12}CO/^{13}CO$ (excess) = 190, showing that at the end of the succession of reactions the surface to which the stable complex was attached contained very

little excess ^{13}C. If the complex had been decomposed after the first reaction, a much lower value for the above ratio would have been expected. This observation provided evidence that the 'stable' complex was not really stable, but constantly changed as reaction proceeded.

Conclusions

The work that has been described shows that a measurable exchange of carbon atoms between CO and Graphon is possible at a temperature as low as 800°, provided that the Graphon sample is subjected to a small amount of burn-off at a low temperature beforehand. The exchange is reversible, that is $^{13}CO + {}^{12}C \rightleftharpoons {}^{12}CO + {}^{13}C$ and at 850° approaches equilibrium. Only a very small fraction of the B.E.T. area is active in the exchange reaction, and this fraction is markedly dependent on the pretreatment of the sample. The activation energy for the exchange in the temperature range 800 to 850° is about 55 kcal/mole.

Deposited ^{13}C can be removed by treatment of the Graphon with O_2. Only a fraction of the deposited ^{13}C can be retrieved by removal of the Type I surface (that is surface which chemisorbs oxygen at 300°), which indicates that the deposited ^{13}C is not confined to this surface. The ease of retrieval decreases with increasing sample burn-off, an effect probably related to the increase in active surface area. ^{13}C deposited at 950° is more difficult to remove than ^{13}C deposited at 850°. It seems likely that exchange at 950° involves sites which are not active at 850°.

References

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DISCUSSION

Dr. B. McEnaney (School of Materials Science, Bath University):—I was surprised to hear that dissociative adsorption of Graphon was not found at 800°, although I do not doubt that this is correct. My reason for surprise is that the thermodynamic equilibrium for the reaction: $2CO = CO_2 + C$ at 800° and normal pressures on β-graphite is such that CO_2 is present at equilibrium. Presumably, therefore, dissociative adsorption is at least possible in principle.

Author's reply:—At 800° K_p for the reaction $CO_2 + C(\beta) = 2CO$ is 7·95 atmospheres (Walker, P. L., jun., Ruskino, F., jun., & Austin, L. G., *Adv. Catalysis*, 1959, **11**, 133) so that at normal pressures, as you point out, the equilibrium mixture contains a substantial fraction of CO_2. At atmospheric pressure, for instance, one anticipates an equilibrium CO/CO_2 ratio of about 8. However, the work described in our paper involves pressures of very much less than atmospheric. At 100 mtorr pressure the equilibrium CO/CO_2 ratio is 60,400, so that even if equilibrium were attained, the CO_2 present would not be detectable.

Dr. D. A. Dominey (Berkeley Nuclear Laboratories, Berkeley, Glos.):—You have apparently ruled out the occurrence of CO chemisorption and disproportionation, both of which may be expected to lead to exchange of carbon between CO and Graphon. What alternative mechanisms are proposed?

Author's reply:—Disproportionation is thermodynamically unlikely under the experimental conditions. No chemisorption of CO was detected in the present experiments, although Miles, who used a much smaller reaction system and lower pressures, did detect a small amount. One presumes that the exchange must proceed by means of an intermediate complex. There is no evidence that the exchange changes the chemical nature of the surface in any way, so a mechanism of the following type is tentatively proposed:

Dr. D. A. Dominey:—An alternative explanation to
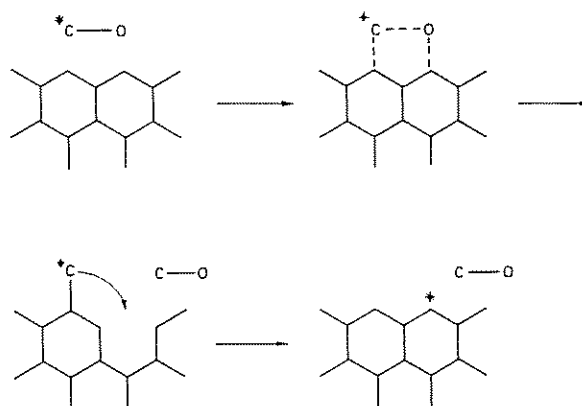
that given in our paper (p. 322) for the fall in the specific activity of gas produced by oxidation at 750° of the non-homogeneously labelled specimen S2 (illustrated in Fig. 2) is suggested by your results which show that 'low temperature gasification of the Graphon surface is required for the production of sites which are active in the exchange reaction'. It seems likely that a similar process occurred during the oxidation of our ^{14}C-labelled graphite during oxidation at 500° and that these sites were then able to react with CO produced during the subsequent oxidation at 750°. The concentration of these sites would decrease in successive oxidations at 750°.

Author's reply:—This explanation does not seem very likely as one would expect the rate of the exchange at 750° to be very much less than the rate of oxidation. However, when we chemisorbed oxygen on a labelled surface at 300° and then decomposed the surface oxide by heating in a closed system at 3°/min up to 950°, comparison of the rates of evolution of [12]CO and [13]CO indicated that at 850° and above, evolved [12]CO was exchanging with ^{13}C sites on the surface.